SUPPORTING INFORMATION

Modelling for understanding the mechanism of the hydrogen peroxide direct synthesis from batch, semibatch and continuous point of view

Nicola Gemo[a], Tapio Salmi[a], Pierdomenico Biasi[a,]*

[a] Department of Chemical Engineering, Åbo Akademi University, Biskopsgatan 8, ÅBO-TURKU, 20500, Finland

* Corresponding author: bpierdom@abo.fi

1. Catalyst preparation

Pd supported on K2621 materials were prepared by ion exchange method. The reduction of the precursors to the metals takes place inside the polymer framework, which is able to control the dispersion, the size and, therefore, the catalytic properties of the metal nanoparticles. Lewatit K2621 is a macroreticular, sulfonated polystyrene–divinylbenzene (SPSDVB) resin.

The resin K2621 was washed with water (300 ml for 10 g of material) and rinsed with methanol (100 ml for 10 g material). 2.0 g of K2621 was suspended in 10 ml of distilled water and left standing for 2 hours. An aqueous solution of $Pd(NO_3)_2$ was added to the suspension. The amount of $Pd(NO_3)_2$ was 0.0174 g with 1.1702 g of K2621 to obtain 0.5 wt.% nominal Pd loadings,

respectively (ICP analysis showed a loading of 0.52 wt.%). After adding the metal solution, the suspension reacted overnight under mechanical stirring (swirling plate). The material was filtered and washed with deionized water (5 x 10 ml). The mother liquors were analyzed for the unreacted metal by means of inductively coupled plasma mass spectrometry (ICP-MS). The residual amount of metal after the ion-exchange was always less than 0.1 mol % of the initial amount, confirming that the actual metal loadings were essentially equal to the nominal values. The as synthesized materials were suspended in THF and reduced under H_2 flux, at room temperature, for 5 hours. After recovery by vacuum filtration, the materials were washed on filter paper with THF (3 x 10 ml) and dried at 110°C overnight.

2. Catalyst characterization

Active metal content in the reaction medium was accessed by a PerkinElmer Sciex ICP Mass Spectrometer Elan 6100 DRC Plus. The timing parameters were: Sweeps/Reading: 11, Readings/Replicate: 1, Number of Replicates: 7, Dwell time: 50.0 ms, Scan mode: Peak Hopping. The calibration solutions were prepared from commercial single element solution for Pd, diluted into standard serial from 1 ppb to 100 ppb.

TEM analyses were carried out with an energy filtered transmission electron microscopy (EFTEM, LEO 912 OMEGA, LaB6 filament, 120 kV). Samples were prepared by suspending a few milligrams of the powder in high purity isopropyl alcohol (or ethanol). After sonication (30 s) a small droplet (5 µl) of the suspension was transferred onto a holey-carbon film coated Cu grids, which was eventually introduced into the microscope.

3. Catalyst Characterization results

The average nanoparticle size of the catalyst obtained with this procedure is 5.2 nm. The particle size distribution is reported in table Fig. S.1

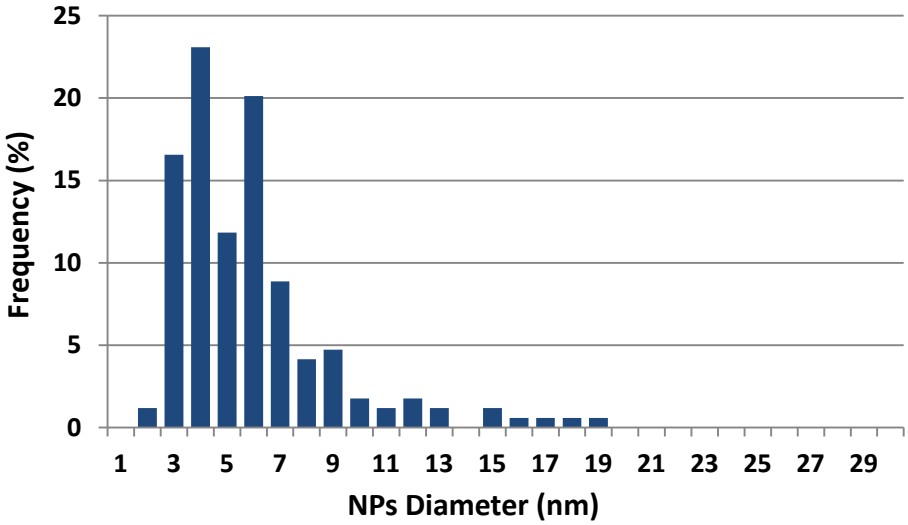
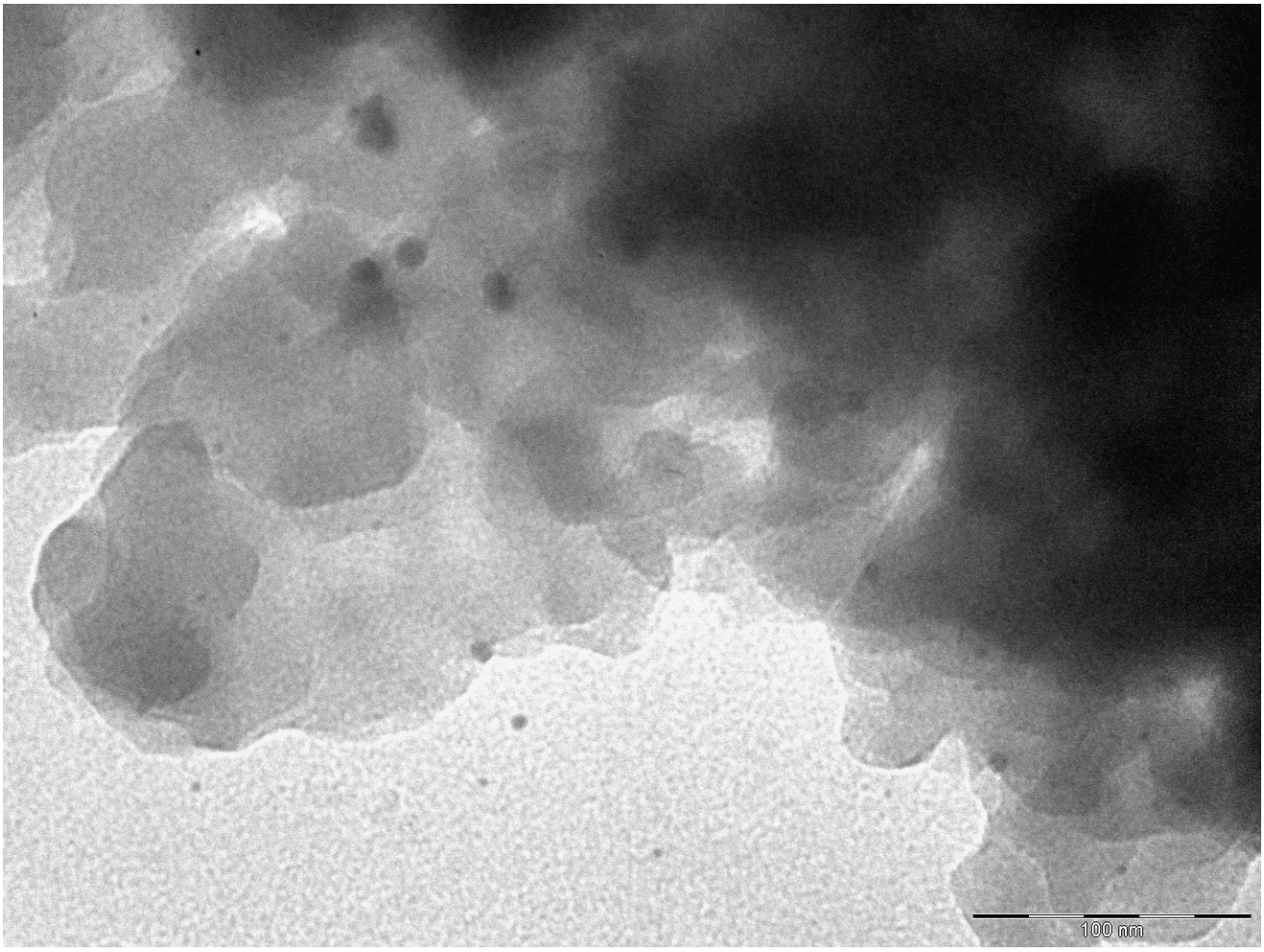
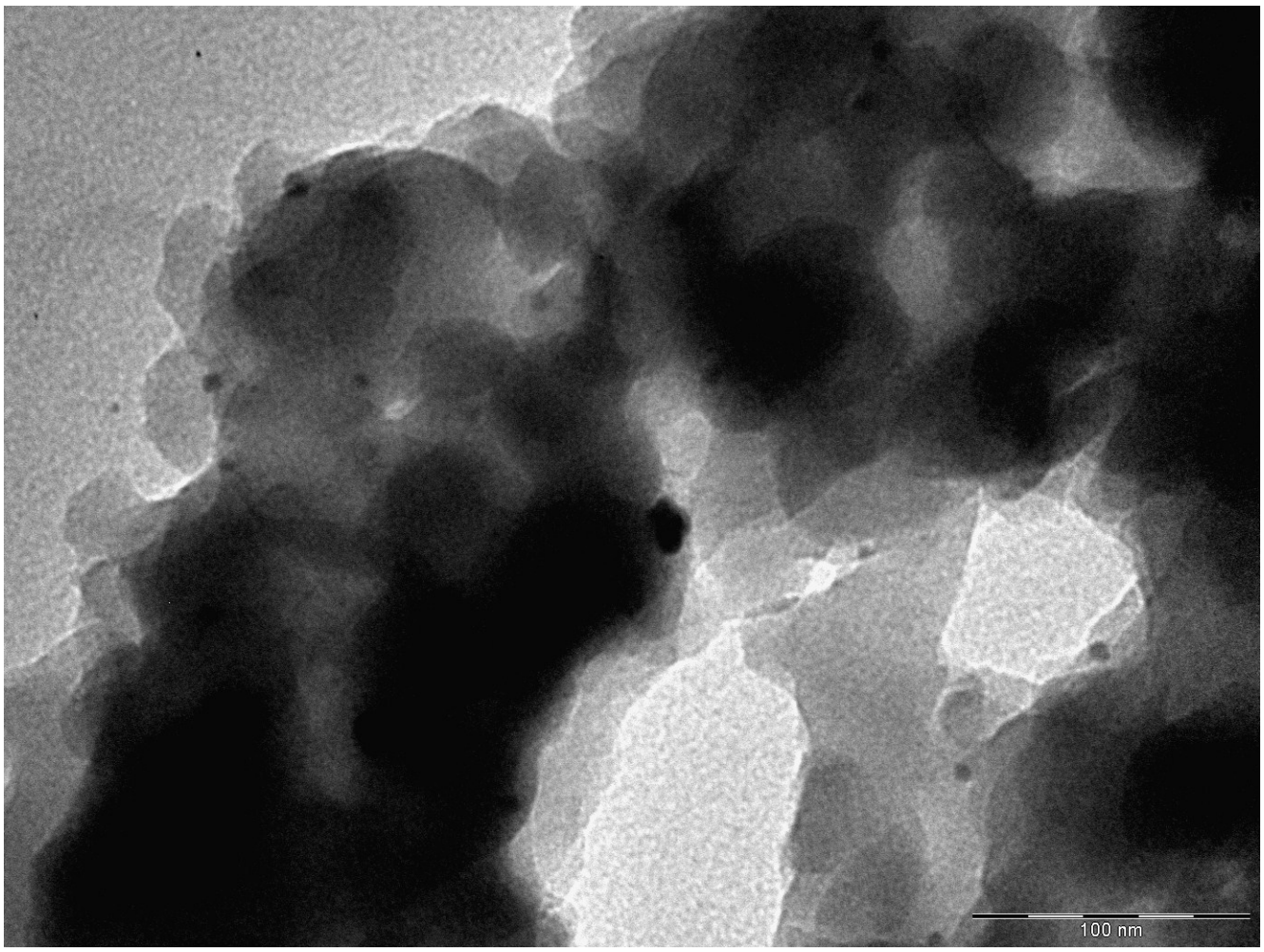
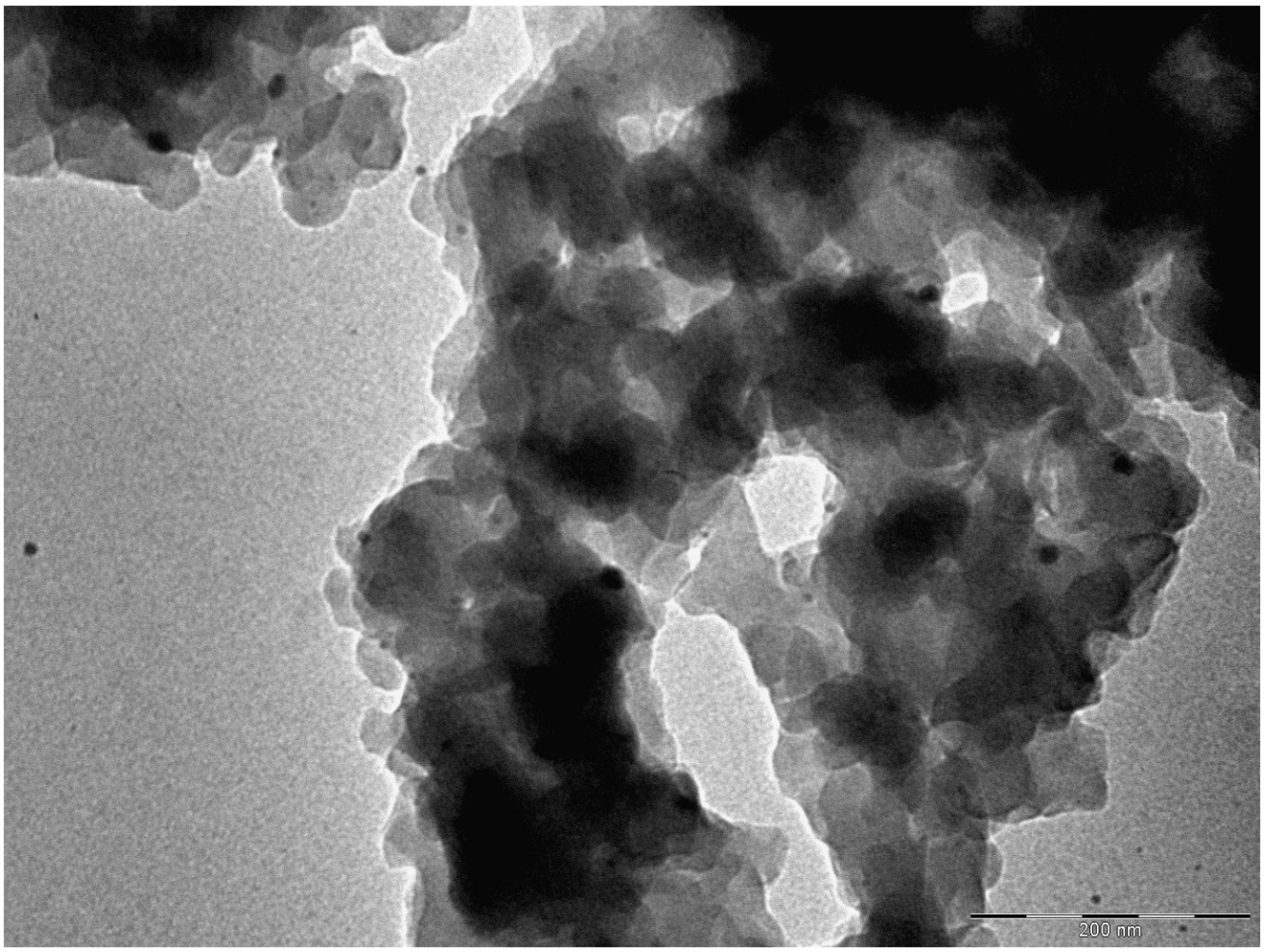


Figure S.1. Particle size distribution of the Pd/K2621 catalyst

TEM images are reported below




100 nm


200 nm

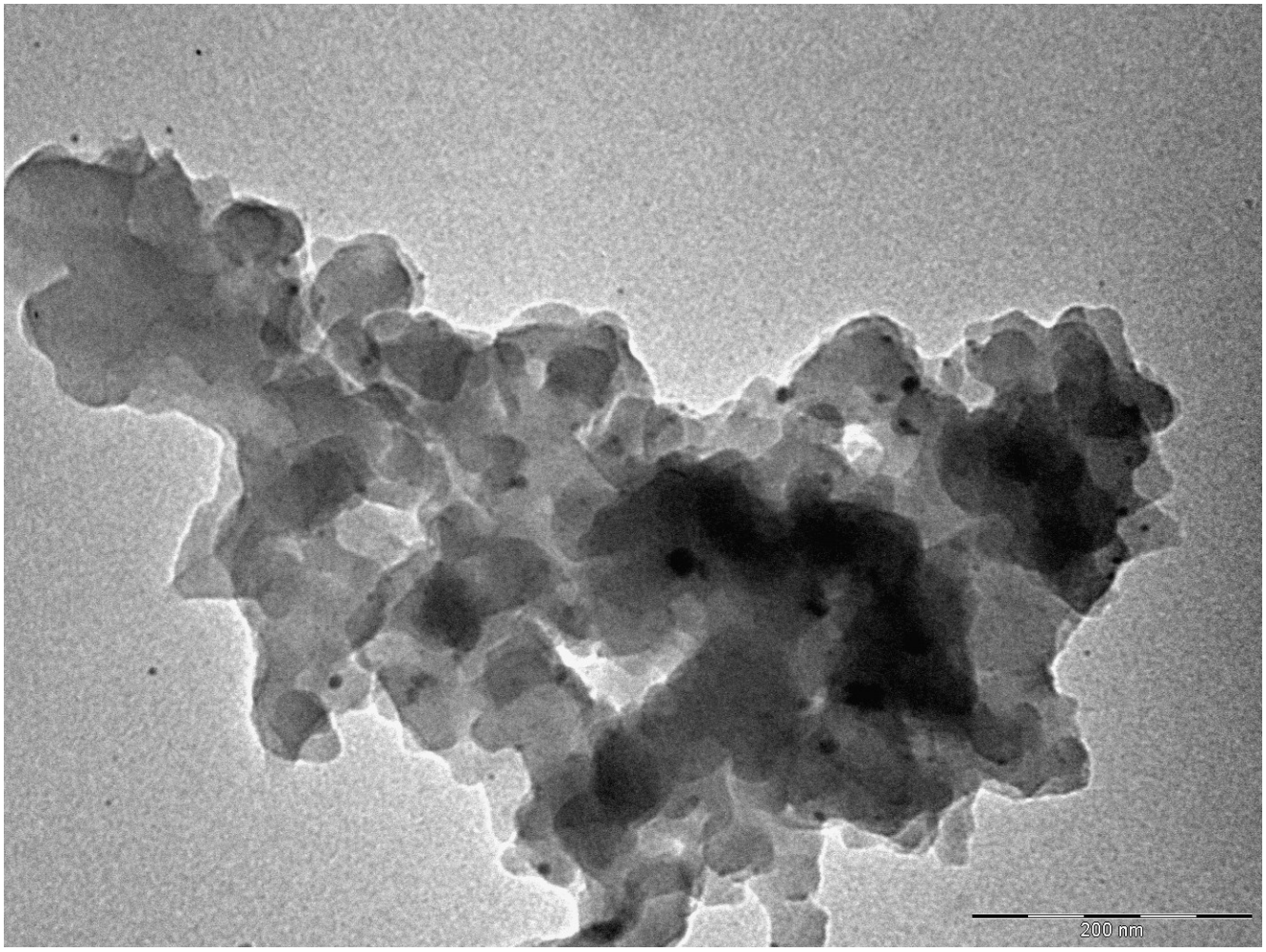


Figure S.2. TEM images of the Pd/K2621 catalyst. Resolution 200k and 100k.

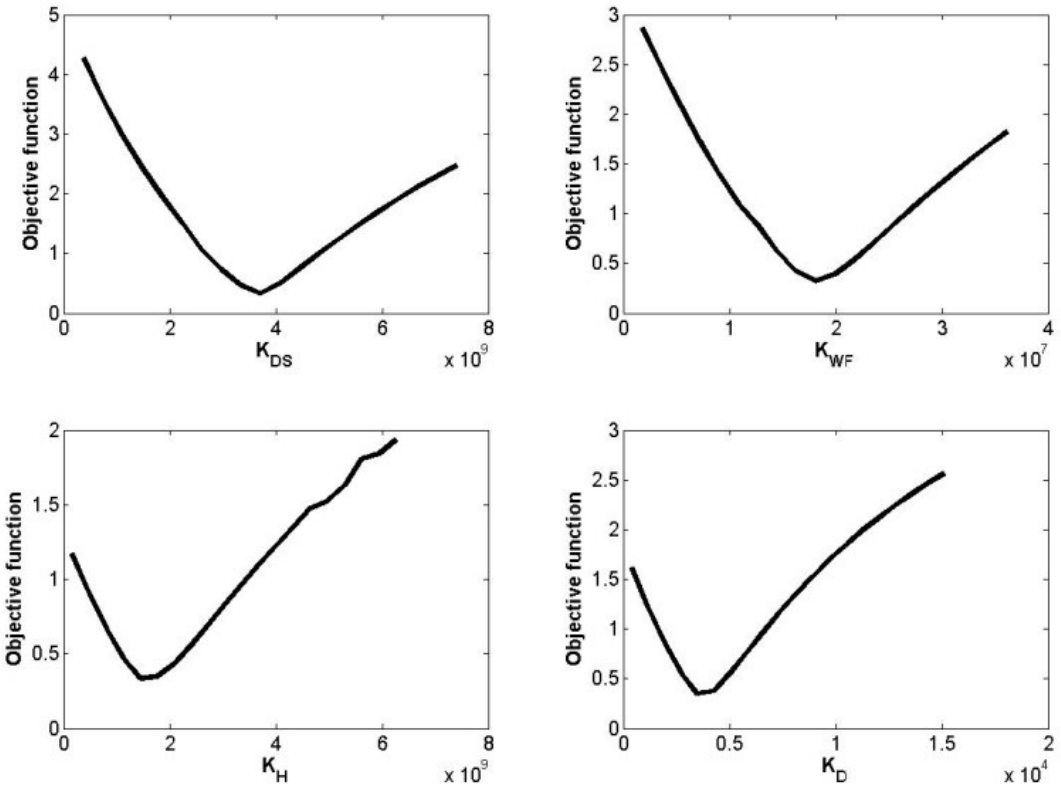


Figure S.3. Sensitivity analysis plots of regressed kinetic parameters (T = 15 °C) in the batch reactor.

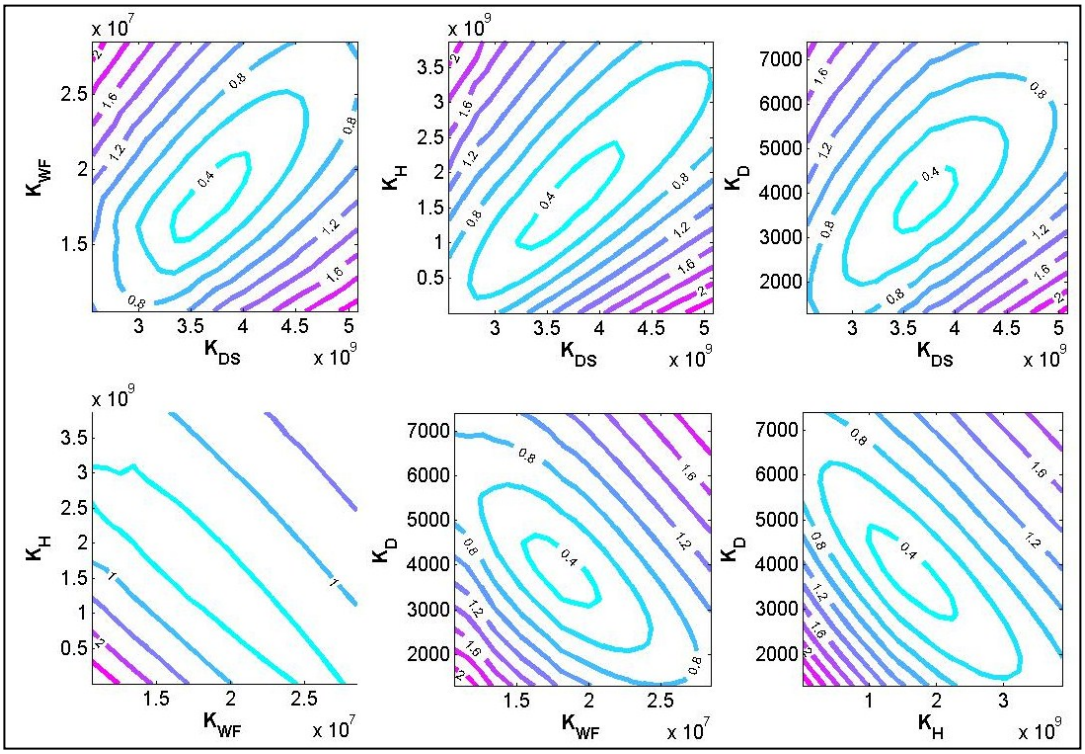


Figure S.4. Contour plots of regressed kinetic parameters (T = 15 °C) in the batch apparatus

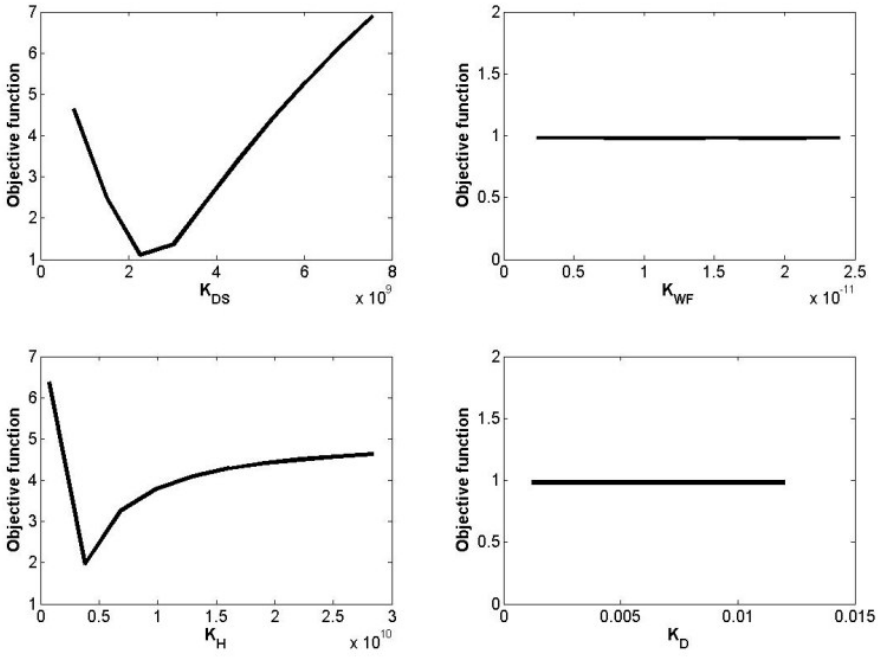


Figure S.5. Sensitivity analysis plots of regressed kinetic parameters (T = 15 °C) in the semibatch reactor

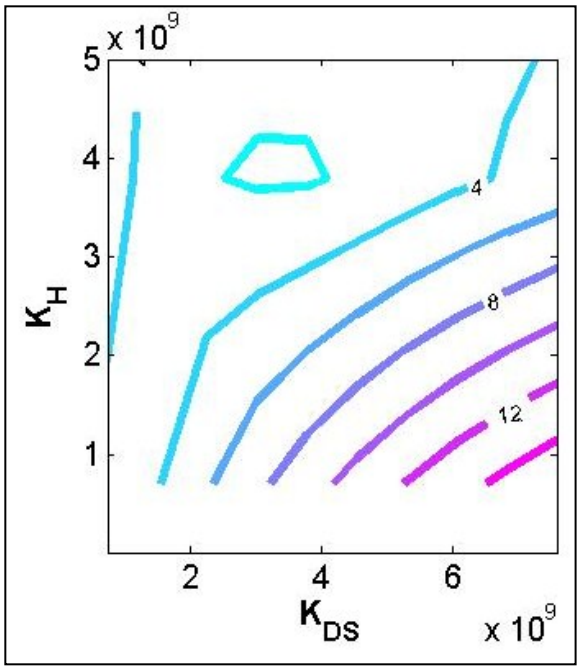


Figure S.6. Contour plots of regressed kinetic parameters (T = 15 °C) in the semibatch apparatus

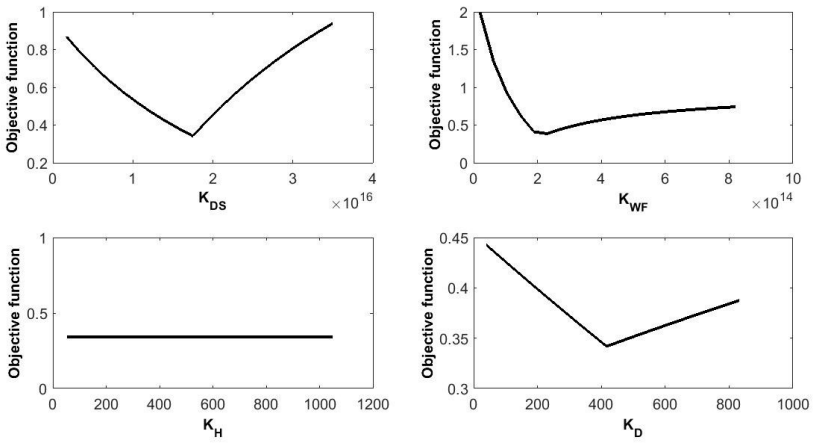


Figure S.7. Sensitivity analysis plots of regressed kinetic parameters (T = 15 °C) in the batch reactor.